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Mechanisms and Processes for Conversion of Smaller boranes to Larger Boranes or Borane Fragments

FINAL REPORT

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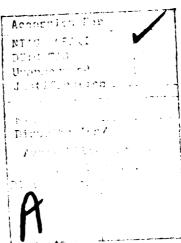
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I. Statement of the Problem

Stock's early syntheses of boron hydrides involved the reaction of a rather poorly defined magnesium boride with aqueous phosphoric acid. 1 Miserable yields of a hydride mixture containing large percentages of higher hydrides were obtained. All subsequent procedures, based largely on the work of Schlesinger, Brown, Burg and their coworkers^{2,3} as well as some commercial programs⁴, gave B₂H₆ as sole initial product. Higher boranes (particularly those needed for the synthesis of carboranes) are currently made from diborane by thermolysis. Through proper selection of reaction conditions and equipment B₄H₁o, B₅H₉, B₅H₁₁, or B₁oH₁₄ can be prepared in fair to good yields⁵, but the processes are very difficult and expensive commercial operations. Three other rather generalized processes for converting B2H6 to higher hydrides have been of interest in recent years. The first of these, studied recently by Hill and Johnson⁶, builds on earlier work of Hough, Marshall, Hunt, Hefferan, Adams and Makhlouf of Callery Chemical Co. The processes involves the pyrolysis of $[R_4N]BH_4$ to yield $[R_4N]_2B_1oH_4o$. This is followed by the opening of the $B_4oH_4o^{-2}$ cage with HCl in liquid $(C_2H_5)_2S$ to give $B_1oH_{1,2} \cdot [S(C_2H_5)_2]_2$. From the latter diethylsulfide adduct, carboranes can be obtained. Yields are marginal.

A second process involves the reaction of NaBH₀ with B₂H₀. Following the early work of Hough and Edwards^R on the reactions of B₂H₀ with sodium amalgam to give NaBH₀ and NaB₃H₈. Gaines showed clearly that B₂H₀ reacts directly with NaBH₀ to give NaB₂H₂ and NaB₃H₆. Muetterties carried the process further ¹⁰ and obtained NaB₁₃H₁₄ from NaBH₀ and B₂H₀ under different conditions. This general process has been developed beautifully in a fundamental sense by Shore and his students who have been able to build up large borane anions in a

stepwise fashion by adding a borane group (Lewis acid) to a B-B bond of selected boron hydride anions. 11 Reactions such as those shown were carried out.

$$B_{4}H_{9}^{-}$$
 + ${}^{1}_{2}B_{2}H_{6}$ \rightarrow $B_{5}H_{12}^{-}$
 $B_{5}H_{8}^{-}$ + ${}^{1}_{2}B_{2}H_{6}$ \rightarrow $B_{6}H_{11}^{-}$

Addition of a proton to the anion generated a neutral borane containing one boron more than the starting material. In some cases $\rm H_2$ was lost. A process developed in recent years by Dunks and Ordonez $^{1.2}$ at Union Carbide also seems to rely on the general reaction between NaBH₄ and $\rm B_2H_6$. $^{1.3}$

The last process of interest might be considered as a generalized form of the preceding reaction in which Lewis bases other than the hydride anion are added to BH3; the borane addition compound thus generated is then allowed to react with diborane. The generalized equation is:

Some years ago Muetterties reported 10 that the reaction of $(CH_3)_2S$ with B_2H_6 at $70^{\circ}C$ gives $(CH_3)_2S \cdot B_9H_{13}$; a number of other conversions have also been reported; still the systematics of the reaction between diborane and lewis base adducts of the boranes are not now well defined. The study performed under the contract focused on the reactions of the base adducts of borane fragments with another reagent. The study has the ultimate goal of delineating the specific reactions by which conversion of one borane to another occurs in the presence of a base catalyst.

II. Summary of the Results

A. Cleavage Processes and Base Catalysis of Borane Condensation.

Many years ago it was shown in this laboratory that Bollo undergoes unsymmetrical cleavage of the double bridge bond of diborane to give the ionic product $[H_2B(NH_3)_2][BH_0]$. Similarly B_0H_1o gives $[H_2B(NH_3)_2][B_3H_0]$ by an unsymmetrical cleavage, more recently it was shown in this laboratory that Bollin gives $\{H_2B(NH_3)_2\}\{B_4H_9\}$, ¹⁶ and that B_6H_9 gives $\{H_2B(NH_3)_2\}\{B_4H_3\}$. Other amines such as N(CH₃)₃ were shown to give symmetrical cleavage of the double bridge. Species such as ${\rm H_3BNR_3}$ and ${\rm H_7B_3NR_3}$ were isolated from ${\rm B_0H_{10}}$ as a result of a summetrical cleavage process. 18 An application of symmetrical cleavage arguments to B_5H_{11} and $N(CH_3)_3$ suggests that the products should be $(CH_3)_3NBH_3$ and (CH₃)₃NB₀H_B, but a number of studies in several laboratories, including this one, failed to verify the prediction. At that time we proposed that the compound (CH $_3$) $_3NB_4H_8$ is unstable to attack by additional (CH $_4$) $_3N$ thus the products isolated represented a complex mixture of secondary products. In a recent ARO supported study in this laboratory, it was possible to prepare (CHA) aNBaHB as a pure substance. 19 Work with pure (Cll3) 3NB4H8 showed unequivocally that the compound is not attacked destructively by (CH3)2N, but that it is attacked readily by acids such as HCl. Further, as predicted by Parry and Edwards. O and subsequently verified by Shore, 21 B₅H₁₁ is a protic acid. Thus reaction procedures which avoid excess $B(H_{1,1})$ at all times in reaction with (CH $_{1}$) $_{3}N$ do give (CH3) aNBH3 and (CH3) aNBaHa as expected.

The reactions of $Me_3NB_6H_6$ have been examined in some detail since they provide considerable insight into the cage expansion processes. Much of the pertinent chemistry can be summarized by the following equations:

$$Me_{3}NB_{4}H_{8} + HC1 \xrightarrow{\text{in THF}} Me_{4}NBH_{3}H_{7} + THF^{*}BH_{3}C1$$
 (1)

$$\frac{\text{In } CH_2Cl_2}{-80^{\circ}}\text{Me }_3\text{NBH}_3\text{H}_6\text{Cl} + \text{THF} \cdot \text{BH}_3$$

$$Me_3NB_4H_8 + NMe_3 \xrightarrow{below} B_4H_8 (NMe_3)_2$$
 (2)

$$\begin{array}{c} \text{Me}_{3}\text{NB}_{4}\text{H}_{B} + \text{Be}_{5}\text{H}_{14} \xrightarrow{\text{below}} \text{Me}_{3}\text{NB}_{3}\text{H}_{7}, & \text{Me}_{3}\text{NB}_{4}\text{H}_{3} \\ & \text{in CH}_{2}\text{C}\ell_{2} - \text{Be}_{6}\text{H}_{10}, & \text{Be}_{5}\text{H}_{9}, & \text{B}_{4}\text{OH}_{10} \end{array}$$
(3)

$$Me_3NB_4H_8 + B_6H_{10} \xrightarrow{room\ temp} B_9H_{15}, B_{10}H_{16}, and others (4)$$

Equation 1, illustrates the reaction of Me $\Delta B_0 H_0$ with a protic acid and demonstrates very clearly that the solvent is important in determining the course of the reaction. Reaction 2, indicates that Me $\Delta B_0 H_0$ behaves as an acid. The integrity of the B_0 unit is retained in this reaction and the bis adduct dissociates back to $B_0 H_0$. NMe $_3$ and NMe $_4$ at room temperature. Reaction 3, like equation 1, can be interpreted as the interaction of Me $\Delta B_0 H_0$ with a protic acid; since, as noted earlier, $B_0 H_{11}$ is a proton donor. The boron framework expands as a result of this process. These observations explain earlier difficulties in the study of the $B_0 H_{11}$ cleavage reaction with NMe $_4$. It also offers insight into earlier observations of Burg who reported in $1962^{1/2}$ that becamethylenetetramine and some other Lewis bases act catalytically in the decomposition of $B_0 H_{11}$ to produce higher boron hydrides including $B_0 H_{10}$, $B_0 H_{11}$, and $B_1 O H_{10}$. The hexamethylenetetramine-tetraborane(8) compound, $(CH_0)_0 N_0 B_0 H_{11}$, has now been characterized in this study and its chemistry is very similar to that of Me $\Delta B_0 H_{10}$.

Reaction 4 above, like reaction 3, shows an intermediate hydride B₀H₁o acting as a proton donor. Alternatively, reaction 4 above may be interpreted as a result of the acid behavior of Me₃NB₆H₁₀ toward the peripheral B-B bond of B₆H₁₀. An intermediate thus produced, Me₃NB₆H₁₀, would split out

Me₃NBH₃ to give B₆H₁₀. It is pertinent to note that both B₃H₁, and B₁oH₁₀

appear as significant products. Further study of these systems is needed, particulatly since B_6H_{10} is produced in considerable amounts in the reaction between B_6H_{11} and $Me_3NB_4H_8$ and would be available for further reaction with $Me_3NB_4H_8$ in the system to give B_4oH_{10} .

- B. The Hypho Series of Boranes and Borane Condensation Reactions.
 - 1. The Classification Scheme.

Formulas, 20 geometry and framework electrons, 20,20,20 have served as the basis for the classification of boron hydrides. The parent B_nH_n —family is called the close series. According to electron counting rules of Rudolph and Wade 24,25 this family has 2n+2 boron framework electrons. The nide series, corresponding to the parent B_nH_{n+n} series, has 2n+4 framework electrons. The arachno series corresponding to the parent B_nH_{n+n} series has 2n+6 framework electrons. Members of a relatively new hypho series with 2n+8 framework electrons have been characterized by Shore 22,20 who first reported the structures of $B_5H_0 \cdot 2PMe_3$ and $B_0H_10 \cdot 2PMe_3$, by Wallbridge 20 , ($B_0H_0 \cdot 2PM_3$, $B_0H_0 \cdot diphos$ and $B_5H_0 \cdot 2PMe_3$), and new members were newly prepared $^{30,+13}$ in this laboratory ($B_0H_8 \cdot 2PMe_3$, $B_2H_5 \cdot 3PMe_3$). A sizable number of new hypho class compounds as well as a few members of a still higher unnamed series with 2n+10 framework electrons have been characterized in the study which is just being completed in this laboratory.

The hypho and higher class compounds are of interest in this study since a species with more skeletal electrons should be more sensitive to acids and to borane acid attack. Specifically an increase in the number of framework electrons increases the number of B-B two center bonds and should thus increase the number of sites which can react with borane acids, usually through an insertion process.

2. Hypho Class Compounds of Balla.

The reaction of excess Me₃N with Me₃NB₄H₈ gives the hypho class $(Me_3N)_2B_4H_8$ which can be isolated below -40° C. Ammonia, monomethylamine, and dimethylamine also add to Me₃NB₄H₈ to give compounds of general formula B_4H_8 NMe₃-Amine, which have been characterized at low temperatures. 19 , $^{3.7}$

Reaction of B₀H₁₁ with PMe₃ gives a hypho compound (h₁₀P)₀B₄H₈, which is stable enough at room temperature to permit purification by sublimation.³⁰ In sharp contrast to the case with Me₃N, the 1:1 phosphine adduct Me₃PB₄H₈ could never be isolated; only the 2:1 hypho class compound, Me₃P)₀B₄H₈ could be obtained. Two other mixed hypho class B₃H₃ compounds were also obtained.³³ by adding one mole of NMe₃ or PMe₃ to B₃H₃Ce.

3. Hypho and Arachno compounds derived from Balla.

As a result of the work of Shore and his students, it was known that the reaction of B₅H₉ with PNe₃ gives the hypho compound B₆H₉·2PNe₃. PNe₃ with excess PNe₃. While it was believed earlier that the reaction of B₆H₉ with excess PNe₃ ultimately gave Me₃PBH₃, studies completed in this laboratory demonstrate conclusively that the reaction of B₆H₉·2PNe₃ or of B₆H₉ with excess PNe₃ gives rise to reactions which can be described by the following equations: ⁴¹

$$B_5H_4^*2PMe_3 + 3PMe_3 + B_2H_4^*2PMe_3 + B_3H_5^*3PMe_3$$
 (5)

$$B_5H_9 + 5PMe_3 \rightarrow B_2H_4 \cdot 2PMe_3 + B_3H_5 \cdot 3PMe_3$$
 (6) (excess)

The $B_2H_0*2PMe_3$ is an arachno species while the $B_3H_6*3PMe_4$ is a new hypho-compound, the only B_3 hypho-compound known. The arachno-compound, $B_2H_0*2PMe_3$, can be sublimed from the reaction mixture. Simultaneously the $B_3H_6*3PMe_4$ converts to a known hypho-compound, $B_6H_1o*2PMe_4$: 28

2 B₃H₅·3PMe₃
$$\xrightarrow{\Lambda}$$
 B₀H₁0·2PMe₃ + 4PMe₃

The compound is identical to the comparable species generated from Ballio and 2PMe₃. Up to this time the Ballio 3PMe₃ has not been isolated as a pure compound because of its decomposition during separation procedures; still, its identity in the original mixture has been unequivocally confirmed. The structure, based on NMR, is:

This compound reacts with HCl in accordance with the equation:

$$B_3H_5$$
, 3PMe $_3$ + 2HC1 $\frac{-80^{9}C}{\text{In CH}_{2}\text{CH}_{2}}$ $\frac{-80^{9}C}{\text{Me}_{3}\text{PBH}_{3}}$ + 2Me $_{3}\text{PBH}_{2}$ CI

We have also explored the reactions of both I-methylpentaborane(9) and 2-methylpentaborane(9) with excess PMe, to see if the identify of the products obtained would provide any clue as to the mechanism of the cleavage process. In both cases the methyl group appeared on the B₂ fragment rather than on the B₃ fragment. The products were CH₃B₂H₃·2PMe₃ and B₃H₅·3PMe₄. Mechanistic interpretations of these facts is found in the appropriate publication. (9) isomerizes to the 2-methyl compound in the presence of a Lewis base.

4. Trimethyl Phosphine Adducts from Bellio.

Pure B_6H_{10} reacts with excess PMe $_3$ as indicated by the equation: $B_6H_{10} + 6PMe_3 + xB_2H_0 + 2PMe_3 + xB_4H_6 + 4PMe_4 + 2(1-x)B_3H_6 + 3PMe_4$

The new compound B_0H_6 4PMe₃ belongs to a new class above hypho (klado) with 2n + 10 framework electrons. The structure assigned on the basis of NMR is

A compound $B_6H_1\sigma \cdot PNe_3$ was also isolated below $-20^{\circ}C_*^{3/2}$. The structure tentatively assigned is:

C. The Reaction Chemistry of B2Ha · 2PMe3.

The compound B₂H₄·2PMe₃ is the simplest borane compound with a B-B bond. It has been studied as a prototype to delineate the chemistry of the two center B-B bond. The compound is easily prepared, as noted in section B, 3 from B-H₄ and PMe₄.

1. Formation of the Triborane Cation, $[B_0H_6(PMe_0)_{\odot}]^{\frac{1}{4}}$ by Unsymmetrical Cleavage of B_2H_6 or B_0H_4o .

Non-symmetrical cleavage of the double bridge bond in B₂H₆ gives H_2B^+ and BH_0^- . The BH_0^- can add BH_0 to give the $B_2H_2^-$ anion. When $B_2H_4 \cdot 2PMe_3$ is treated with an excess of B_2H_6 in CH_2CI_2 at $-20^{\circ}C$, a reaction occurs which can be described by the following equation:

$$B_2H_4 \cdot 2PMe_3 + \frac{3}{2} B_2H_6 \rightarrow [B_3H_6 (PMe_3)_2]^+ [B_2H_2]^-$$

At least in a formal sense the reaction can be viewed as a non-symmetrical cleavage of the double bridge bond of ByHa, with addition of the ${\rm H_2B}^\pm$ unit to the B-B two center bond.

Similarly B₄H₁o is cleaved non-symmetrically by B₂H₆·2PMe₃ to give $[B_3H_6(PMe_3)_2]^{\frac{1}{2}}[B_3H_6]^{\frac{1}{2}}$. The cation is isoelectronic with the B₃H₆ anton and

is assigned a structure similar to the Bulba structure.

The cation, like $B_3H_8^{-}$, 39 is fluxional. At -70° C the motion is slow enough to observe the ^{11}B and ^{1}H NMR signals of the static structure. The cation is resistant to strong acids, as the following equation illustrates: 39

The decomposition of $[B_2H_0](PNe_3)_2[^{\dagger}(B_2H_2)^{\dagger}]$ on warming can be best described by the following equation:

 $[B_3H_6(PMe_3)_2]^+[B_2H_7]^- \xrightarrow{\Lambda} Me_3PB_3H_7 + Me_3PBH_3 + {}^{1}_2B_3H_6$

The process can be viewed as transfer of an H^- back to the cation from the anion with loss of a PMe $_3$ from the cation to the BH $_3$ formed.

The compound $[B_3H_6(PMe_3)_2]^+[B_3H_8]^-$ is sensitive to strong bases such as NMe3. The equation is:

 $[B_3H_6(PMe_3)_2]^+[B_3H_8]^- + NMe_3 \rightarrow Me_3PB_4H_8 + Me_3PBH_4 + Me_3NBH_3$ This process can be viewed as transfer of a hydride ion to the cation to generate $B_2H_4 \cdot 2PMe_3$ and BH_3 , the latter being combined with NMe₃ to give Me_3NBH_3 , followed by interaction of the $B_2H_4 \cdot 2PMe_3$ with the B_3H_2 fragment in the system.

Methyl and fluoro derivatives of the cation were also prepared during the past grant period. The compounds are: $^{311},^{\prime10}$

 $[CH_{2}B_{2}H_{5}(PMe_{3})_{2}]^{+}[B_{2}H_{7}]^{-}$, $[CH_{3}B_{3}H_{5}(PMe_{2})_{2}]^{+}[B_{3}H_{5}]^{-}$ and $[B_{3}H_{4}F_{2}(PMe_{3})_{2}]^{+}[B_{2}F_{7}]^{-}$.

2. Attempted Unsymmetrical Cleavage of B_5H_{11} by B_7H_9 (PMe₃)₂.

As noted above $B_2H_4 \cdot 2PMe_3$ will cleave both the B_2H_6 and B_4H_{10} molecules unsymmetrically to give the $\left[B_3H_6\left(PMe_3\right)_2\right]^+$ cation and the anion characteristic of unsymmetrical cleavage of that borane. Since it is known that B_5H_{11} will undergo non-symmetrical cleavage with NH_3 to give the B_4H_3 anion, it was expected that $B_2H_4 \cdot 2PMe_3$ should interact with B_5H_{44} as indicated by the following equation:

quation:

$$B_2H_4 \cdot 2PMe_3 + B_5H_{14}$$
 $\xrightarrow{-80^{\circ}C}$ $(B_3H_6 (PMe_3)_{\odot})^{+} [B_3H_6]^{-}$
 CH_2Cl_{\odot}

No evidence for the formation of the B_0H_0 ion could be found. Instead, a process as defined by the following equation occurs:

$$B_2H_0 \cdot 2PMe_3 + B_0H_{14} - \frac{-80^{\circ}C}{CH_2CL_3} \cdot {}^{11}B_0H_{12} \cdot PMe_3!! + Me_0PBH_3$$

$$above_{-40}{}^{\circ}C$$

$$B_0H_9 \cdot PMe_3 + \frac{1}{2}B_2H_6$$

$$B_0H_9 + Me_3PBH_3$$

The B_6H_{12} -PMe₃ and B_5H_9 -PMe₃ are new compounds. Characterization of the B_5H_9 -PMe₃ has been completed⁴⁰ and that of B_6H_{12} -PMe₃ is being pursued.

3. The Reaction of $B_2H_4 \cdot 2PMe_3$ with $B_3H_7 \cdot THF$.

The observed reaction is given by the equation: 4O $B_2H_4 \cdot 2PMe_3 + THF \cdot B_3H_7 \xrightarrow{25^{O}C} B_4H_8 \cdot PMe_3 + Me_4PBH_4 + THF$

A borane expansion process is observed.

D. Newly Prepared Borane Adducts.

As described in the foregoing sections a number of new types of borane compounds have been prepared and characterized in the past year. The list

includes: B₃H₅·3PMe₃(hypho class), B₆H₆·4PMe₃(klado class), B₆H₄₂·PMe₃(arachno class), B₆H₁₂·PMe₃(hypho class). The current situation is put into focus by examination of Table I which shows the types of known boranes and borane adducts and the new compounds added in this investigation.

Other new chloro compounds prepared include LB₃H₆Cl, 19,32,44 where L = NMe₃, NH₃, CH₃NH₂, (CH₃)₂NH, PH₃, and PMe₃. The adducts are sensitive to bases. The THF adduct could not be prepared.

Further the series LB₃H₇ was prepared where L = PH₃, MePH₂, Me₂PH, Me₃P. The chemistry of this family was contrasted with that of the series LBH₃. 43,44 Differences are explained by the greater acidity of B₃H₇. The fluxionality of hydrogens in the B₃ framework becomes greater (appears at lower temperature) as the strength of the base increases. See also ref. 45.

L	≈ 1	2	3	4	Ţ.	= J	2	3	4	Į,=	=	2	3	4
внз	Х		Γ		(BH ₅)					(BH ₇)				
B ₂ H ₄		Х			B ₂ H ₆	X				(B ₂ H ₈)				
B ₃ H ₅			0		B3H7	0				ВзНэ				
B4H6				0	B4H8	8	8			B4II10				
B ₅ H ₇					B ₅ H ₉	0	Х			B51111	0			
B ₆ H ₈			T		B6H10	0	Х			B ₆ H ₁₂	0			
B7H9					B7H11					ВоН13				
BeH10			Г		B ₈ H ₁₂	X				Bell ₁₄				
B9H11					B9H ₁₃	X				B9H15				
B ₁₀ H ₁₂	Х	X			B10H14	Х	X			B ₁₀ II ₁₆				
B11H13					B ₁₁ H ₁₅					B ₁₁ H ₁₇				
B12H14					B ₁₂ H ₁₆					B ₁₂ H ₁₈				

X - Adducts that had been known prior to the past grant periods.

O - Adducts that were discovered during the past grant periods.

Adducts that had been known and to which new compounds were added during the past grant period.

E. The Deuteration of Triborane Adducts.

THF+B₃H₇ or Me₃NB₃H₇ will react with DC1 at -80° C in CH₂Cl₂ to give either THF+B₃D₇ or Me₃NB₃D₇. The THF adduct can be converted to NaB₃D₈, ⁴⁷ which can be coverted to ND₄B₃D₈. The latter compound has potential interest as a portable D₂ source.

F. Attempted Conversion of Bollo to BroHra.

Earlier, during the course of halotriborane chemistry study, it was found that the treatment of $B_3H_8^-$ ion with BCl₃ resulted in the formation of $B_4H_{10}^{3,2}$. The halogenation by BCl₃, which was effective for the preparation of Me₃NB₃H₆Cl from Me₃NB₃H₇, could not be achieved for the hydride adduct of B_3H_7 , $B_3H_8^-$. The reaction appeared to have proceeded by the abstraction of H^- by BCl₃ to give $HBCl_3^-$. The B_3H_7 group thus freed was thought to undergo a reaction to form B_4H_{10} ;

$$2 B_3 H_7 \longrightarrow B_4 H_{10} + (B_2 H_4)$$

The application of the hydride abstraction reaction to the B_0H_8 ion was intended in hope of producing " B_0H_9 " which might dimerize to give $B_{10}H_{10}$. Indeed, the treatment of $Me_0NB_0H_8$ with excess BCl_3 in CH_0Cl_9 gave $B_{10}H_{10}$. The yield was judged to be fair to good on the basis of the $^{-1.1}B$ NMR spectra of the reaction products. The use of KB_0H_8 , instead of the Me_0N salt, resulted in the formation of a new compound $B_0H_8 \cdot BCl_{10}$. The appropriate equation for the reaction is:

$$KB_SH_B$$
 + $BC1_A$ ---- $KC1$ + $B_CH_B \cdot BC1_{2A}$

The ^{14}B and ^{1}H NMR spectra of the new compound indicated that the BCl₂ unit is inserted at the basal B-B position in the manner similar to that has been found for $B_5H_8 \cdot BMe_2 \cdot ^{48}$. The compound is of interest as an intermediate for the formation of higher borane species, in particular $B_{10}H_{10}$. The work is to be continued.

III. Publications and Technical Reports.

- a. "Isolation and Characterization of Trimethylamine-Tetraborane(8)."
 G. Kodama and A. R. Dodds, 3rd International Meeting on Boron Chemistry,
 Ettal/Munch, FRG, July 1976.
- b. "Reactions of Pentaborane(11) with Methylamines." R. W. Farry and G. Kodama, 3rd International Meeting on Boron Chemistry, Ettal/Munch, FRG, July 1976.
- c. "Reactions of Trimethylamine-Triborane(7) and -Tetraborane(8) with Anhydrous Hydrogen Chloride." A. R. Dodds and G. Kodama, 172nd National Meeting, Amer. Chem. Soc., San Francisco, California, September 1976.INOR 90.
- d. "Methylamine Adducts of Trimethylamine-Tetraborane(8)." A. R. Dodds and
 G. Kodama, 173rd National Meeting, Amer, Chem.Soc., New Orleans, Louisana,
 March 1977. INOR 48.
- e. "Reactions of Tetraborane(10) with Mono-and Dimethylamine." A. R. Dodds and G. Kodama, Inorg. Chem., 1977, 16, 2900.
- f. "Deuteration of Triborane(7) Adducts with Anhydrous Denterium Chloride." Inorg. Chem., 1977, 16, 3353.
- g. "Preparation and Properties of Bis(Trimethylphosphine)-Tetraborane(8)."33rd Northwest Regional Meeting, Amer.Chem.Soc., Seattle, Washington, June 1978.
- h. "Reactions of Hexamethylenetetramine with Boranes." H. Kondo and G. Kodama, Inorg. Chem. 1979, 18, 1460.
- i. "Isolation and Characterization of Trimethylamine-Tetraborane(8)." A. R. Dodds and G. Kodama, Inorg. Chem., 1979, 18, 1465.
- j. "Phosphine and Methylphosphine Adducts of Triborane(7)." V. L. Bishop and
 G. Kodama, 4th International Meeting on Boron Chemistry, Salt Lake City/
 Snowbird, Utah, July 1979. Paper No. 39.
- W. "Hypho-Tetraborane Compounds Containing Carbon Monoxide and Phosphine."
 G. Kodama and R. W. Parry, 4th International Meeting on Boron Chemistry,
 Salt Lake City/Snowbird, Utah, July 1979. Paper No. 45
- "Deuterated Sodium Octahydrotriborate(1-)." M. A. Nelson and G. Kodama, Inorg. Chem. 1979, 18, 3302.
- "Bis(Trimethylphosphine) Adduct of Tetraborane(8)." M. Kameda and G. Kodama, Inorg. Chem., 1979, 18, 3302.
- "Unsymmetrical Cleavage of Boranes by Bis(Trimethyl-phosphine)-Diborane(4).

 Formation of a Triboron Cation." M. Kameda and G. Kodama, J.Am.Chem.Soc.,

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- o. "Cleavage of Pentaborane(9) by Trimethylphosphine." M. Kameda and G. Kodama, 35th Northwest—5th Biennial Rocky Mountain Joint Regional Meeting, Amer. Chem.Soc., Salt Lake City, Utah, June 1980.
- P. "A Cleavage Reaction of Pentaborane(9). Formation of a New Hypho Triborane Adduct." M. Kameda and G. Kodama, Inorg. Chem., 1980, 19, 2288.
- 9. "Reactions of Trimethylphosphine Adducts of Diborane(4) with Boranes."
 M. Kameda and G. Kodama, 2nd Chemical Congress of the North American Continent,
 Las Vegas, Nevada, August, 1980. INOR 75.
- "Trimethylamine-Tetraborane(8), Methylamine Adducts of triborane(7) and Related Chemistry." Ph.D. Dissertation, University of Utah, 1980.
- s. "Formation of the 1:1 Phosphine Adducts of Hexaborane(10)." M. Kameda and G. Kodama, Inorg. Chem. In press.
- t. "Triborane(7) Adducts of Phosphine and Methylphosphines." V. L. Bishop andG. Kodama. Submitted to Inorg. Chem.
- u. (Manuscripts for eight other papers are in preparation and will be submitted to appropriate journals.)

IV. Participating Scientific Personnel.

Robert W. Parry, Professor of Chemistry

Goji Kodama, Research Professor of Chemistry

Alan R. Dodds, Graduate Student, Research Assistant, Ph.D., 1980

Mitsuaki Kameda, Research Fellow

Vicki L. Bishop, Graduate Student, Research Assistant, M.S., 1979

Mansel A. Nelson, Undergraduate Student, Research Assistant, B.S., 1978

Steve A. Snow, Graduate Student, Research Assistant

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